Advanced Accelerator Applications Separations Projects at ORNL

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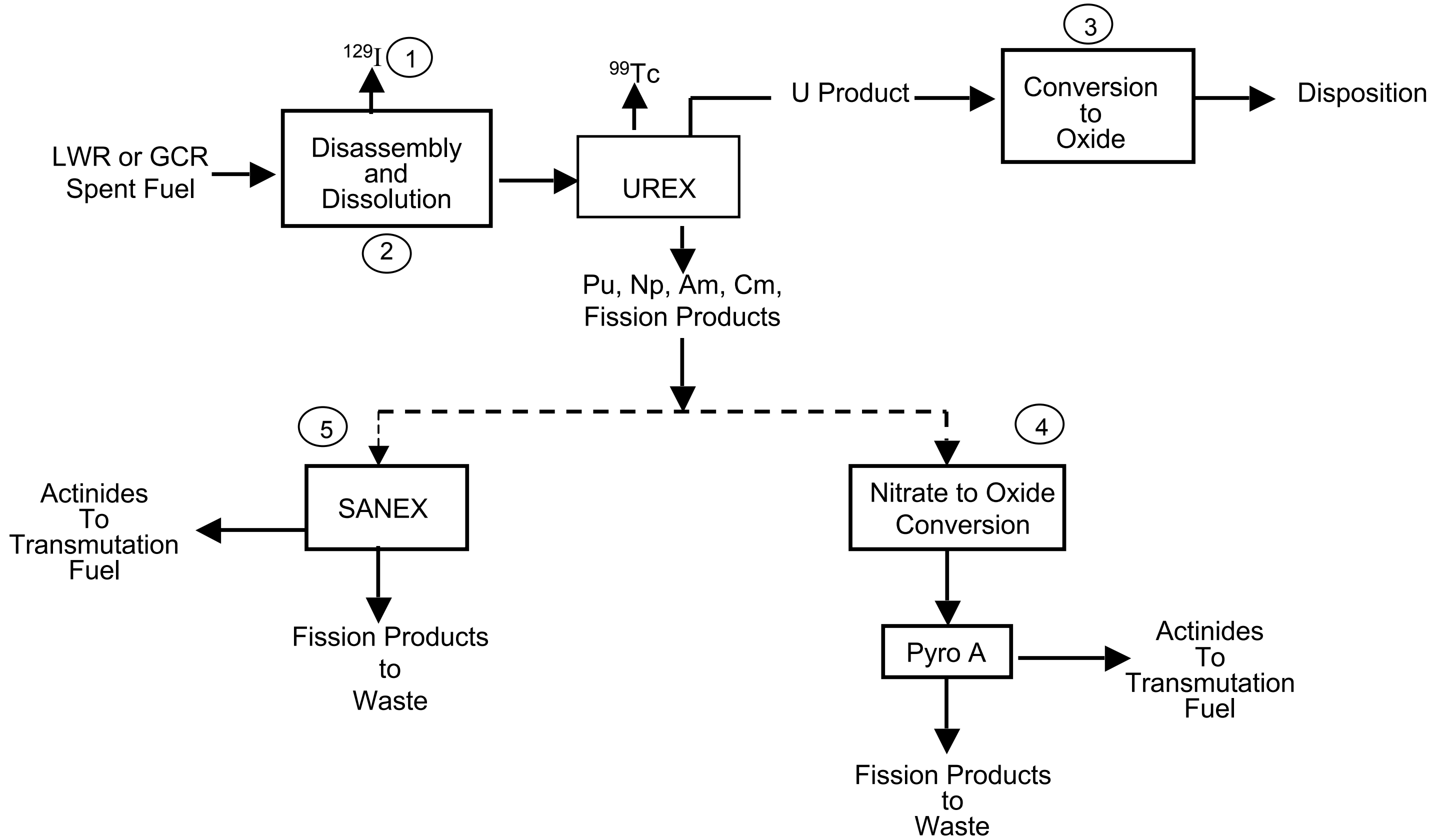
AAA Separations Projects at ORNL



1. **Removal of ^{129}I and conversion to sodium iodide target for transmutation**
2. **GCR Spent Fuel (TRISO-coated) disassembly and dissolution**
3. **Conversion of uranium nitrate to oxide for disposition**
4. **Conversion of UREX raffinate from nitrate to oxide**
5. **Evaluation of new European solvent extraction processes for actinide separation**

Previous ORNL Experience with Isolation of Radioiodine

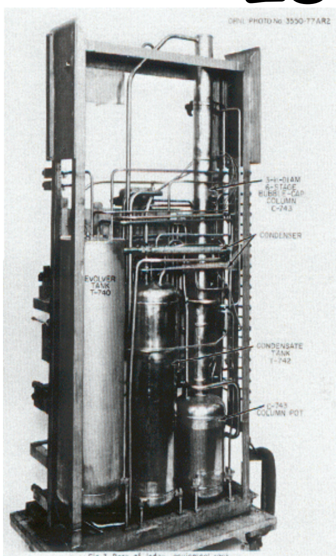
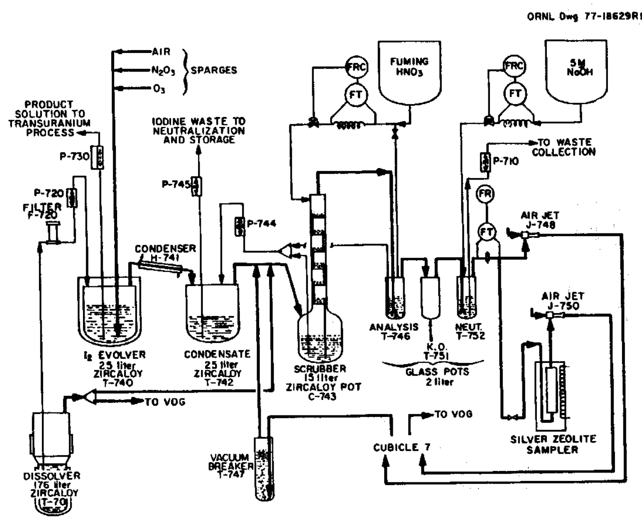
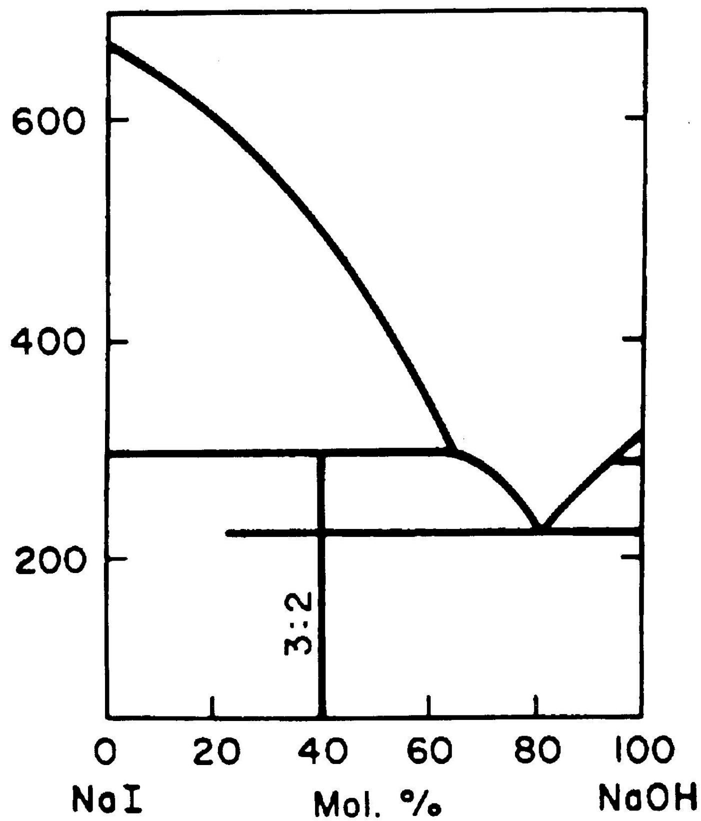


Fig. 3. Back of Iodox equipment rack.



- Iodine removal and capture were studied in high activity tests conducted in 1979
- A special equipment rack was designed and installed in REDC Building 7920, Cell 7. This equipment is still used in current work
- The process shown in the diagram was used. Iodine sorption reagents tested have included (1) fuming nitric acid, (2) mercuric nitrate, and (3) sodium hydroxide
- Results were reported in ORNL/TM-6182 "Iodox Process Tests in a Transuranium Element Campaign", E. D. Collins and D. E. Benker (June 1979)

Proposed Process to Isolate NaI



Guiseppe Scarpa, Atti reale accad. Lincei, Sez. ***I*, 24**, 961 (1951)

- Purpose: to develop a method of scrubbing iodine-containing gases (e.g. I_2, HI, or CH_3I) from fuel processing off-gas streams via reaction and dissolution in molten salts
- The phase diagram of the NaOH/NaI system indicates that at sufficiently high iodine concentration, NaI precipitates as a relatively pure solid phase as the melt is cooled
- Tasks to be performed
  - Experimentally demonstrate the efficacy of iodine trapping by molten NaOH
  - Demonstrate the NaI precipitation
  - Thermodynamic analysis of baseline gas processing scenarios
- Advantages of iodine trapping in molten salts
  - Potentially a simple "one-step" process that enables trapping and NaI product generation in a single trap
  - No aqueous liquid waste
  - Associated conversion on NO_x gases to nitrogen and water vapor by the addition of hydrogen to gas stream
  - Possible direct conversion of CO_2 to simple carbonates
  - NaI product is reference state material and formed directly in the process
  - Isolation of NaI product by simply cleaving solid NaI from solidified salt mass, crystal "pulling" or by sublimination of NaI (to be determined)

The NaOH melt system provides a means of trapping HI or I_2 with the formation of NaI as a primary phase component (H_2 would be added to I_2-containing streams.

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Iodine Trapping in Molten Salts
Progress

Previous

- Demonstrated phase segregation and separation of KI from KOH in analogous, but simpler, salt system.
- Demonstrated phase separation and separation of NaI from NaOH but hampered by subsolidus 3:2 NaI/NaOH compound formation. (See phase diagram).
- Established analytical means for measuring iodide concentration along with the direct aqueous titration of remaining hydroxide content.

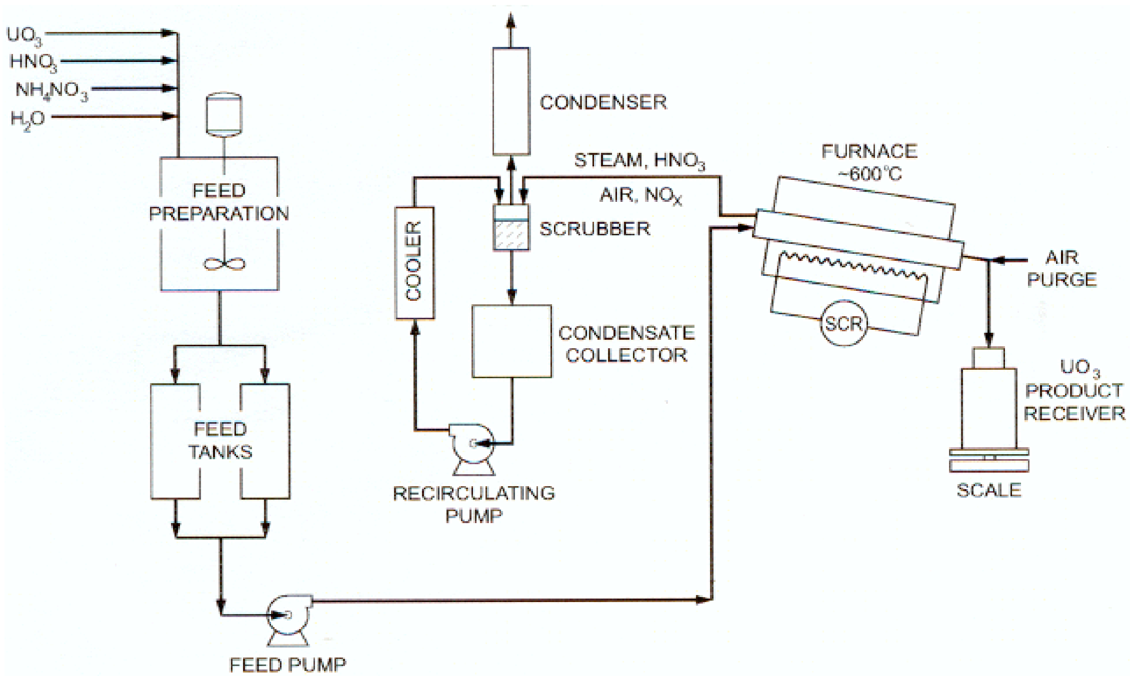
Recent

- Trapping of I_2 vapors in NaOH melt as a function of temperature.
- Examined trapping of I_2 vapors by mixing with 4% H_2/Argon to effect reduction to HI during trapping in NaOH melt.
- Up to 90% of Iodine vapors trapped when melt was at ~600^{o}C.
- Only ~30% I_2 trapped when melt was ~400^{o}C.
- H_2/I_2 reaction apparently requires higher temperatures to first produce HI.

Future

- Test trapping of HI and CH_3I in molten NaOH — FY 2002
- Investigate effects of NO_x and CO_2 contaminant gases — FY 2002
- Improve NaI separation process by: — FY 2003
  - Finer cooling/quenching control
  - NaI crystal pulling from melt
  - NaI sublimation

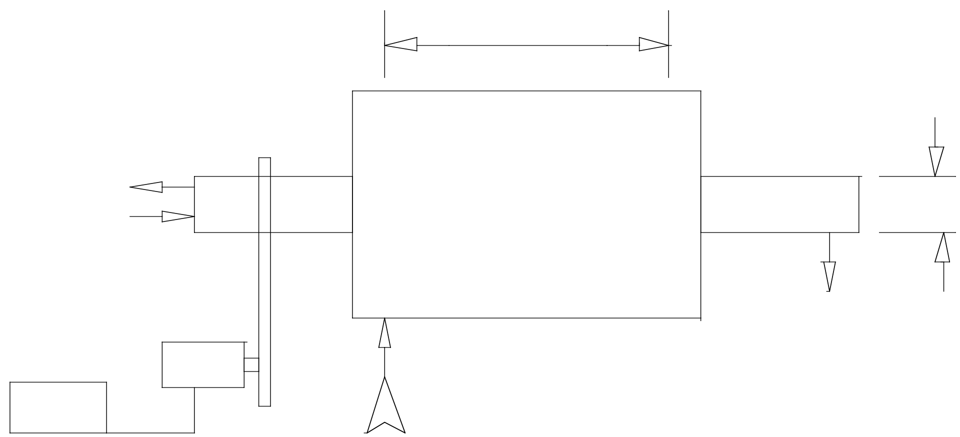
Modified Direct Dentrification for UREX Uranium Product



Developed at ORNL for UO_3-PuO_2 production for Fast Breeder Program. Process has been scaled-up to UO_3 (UO_2) production for AVLIS Program. Units with capacity of 1 kg/hour have been tested. Larger equipment (10 kg/h) unit design and built.

Modified Direct Denitration for UREX Raffinate (Pu-MAs-FPs)

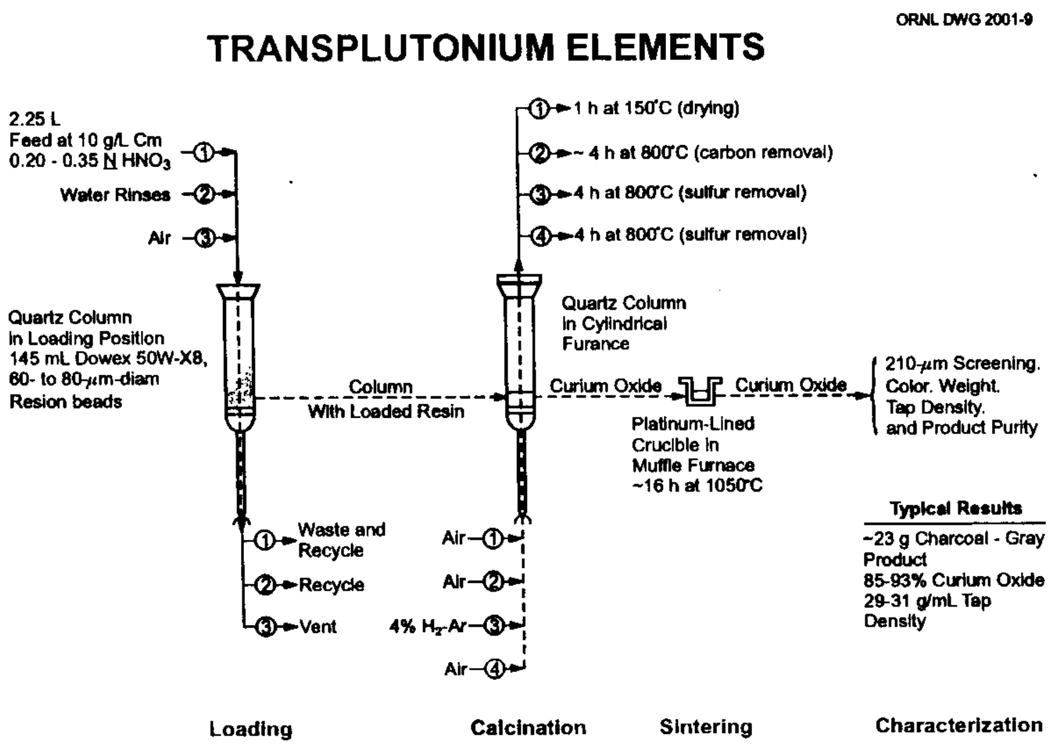
- A conceptual design of a scaled-down (~50–100 g/h) rotary kiln unit was completed
- Design parameters were established to keep the equipment sizes appropriate for glove box operation



Modified Direct Denitration

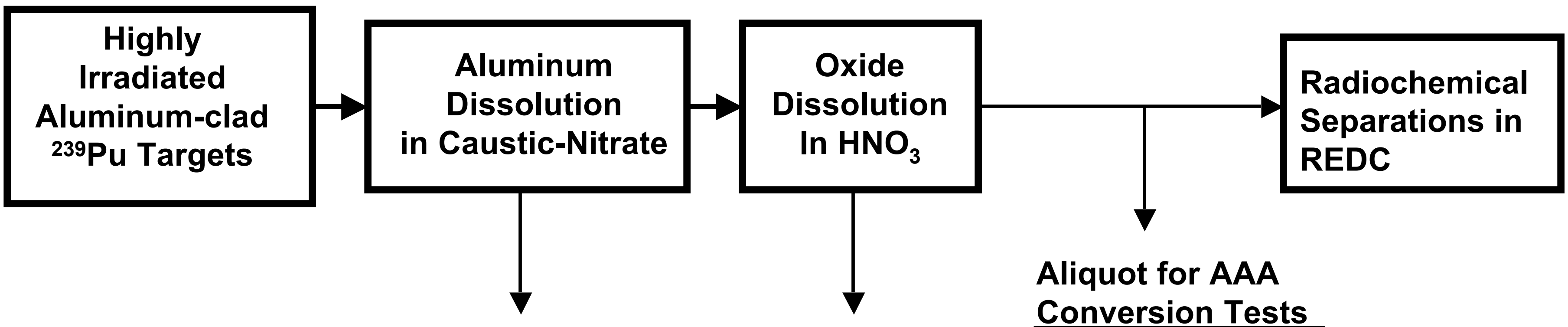
- A commercial vendor reviewed the design parameters and preliminary equipment design and provided a reasonable cost estimate for fabrication
- A purchase order was issued for the unit with delivery expected in early July
- Cold testing of the unit will be done with rare earth surrogates in FY 2002
- Kiln unit will be installed in a glove box for testing and demonstration with Pu, Np, MAs, FPs, and SX residues in FY 2003

ORNL Experience with Resin Loading/Calcination Process



- Used for 25+ years to produce Am-Cm oxide for use in HFIR targets. Current process converts 22 g batches
- Resin loading/calcination process to be scaled-up for other applications. Tests have been run for producing ^{237}Np oxide for ^{238}Pu production.

High Activity Pu-MA-FP Solution for AAA Conversion Tests



Al, Cs

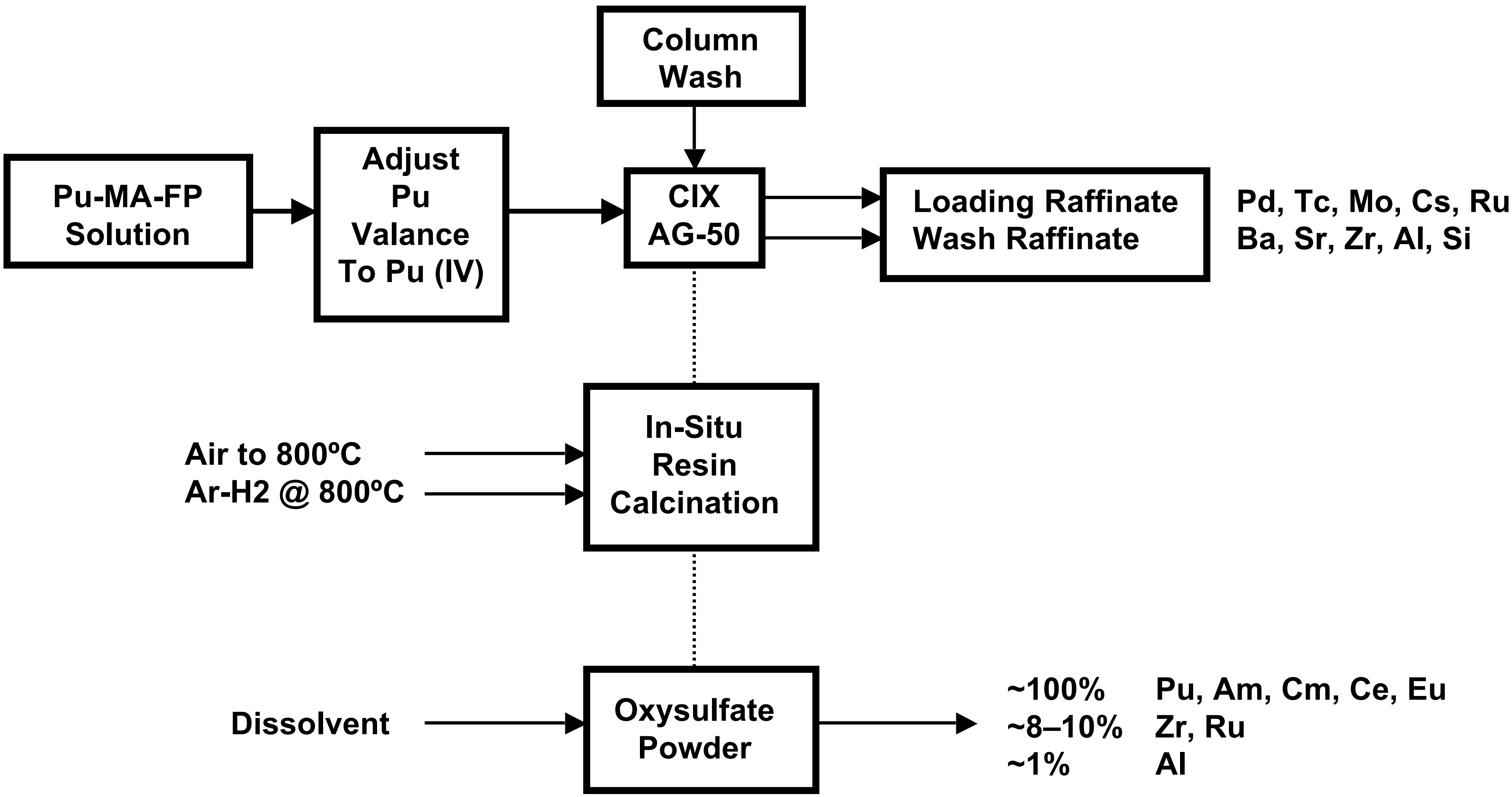
Insolubles
Si
Noble Metals

Aliquot for AAA Conversion Tests

Pu	1395 mg
Am	~350 mg
Cm	190 mg
Np	Not Present
^{137}Cs	390 mCi
^{106}Ru	41 mCi
^{144}Ce	34 mCi
^{154}Eu	566 mCi

Al, Sr, Zr, Mo, Tc, Pd, Ba, Gd

Test Run in FY 2002 on Simulant UREX Raffinate



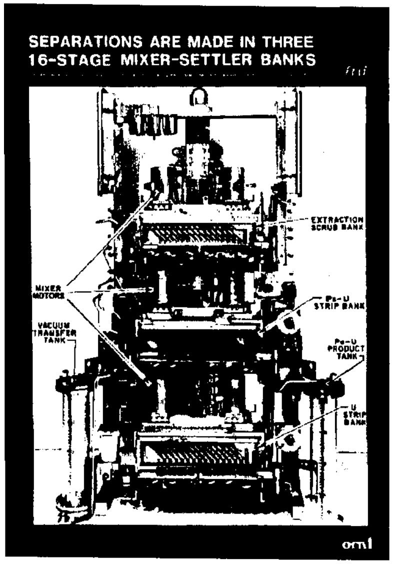
Evaluation of SANEX Extractants Developed in Europe

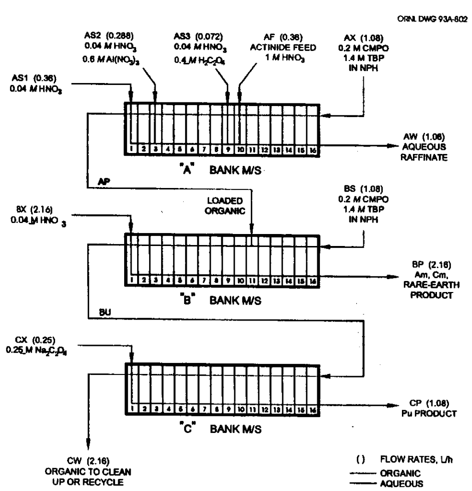
- The SANEX(IV) reagent, bis(chlorophenyl) dithiophosphinic acid developed at ITU has been successfully synthesized at ORNL
- Our initial tests will be with this reagent and the phenyl dithiophosphinic acid reagent which we have obtained commercially
- A draft experimental plan has been prepared and a process solution containing Am/Cm and associated fission products has been selected as the feed material for the extraction testing
- Tests will be done in FY 2002

Future SANEX Evaluations

- ORNL is investigating the synthesis of the SANEX(III) reagent, 2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)-pyridine (BTP) developed at CEA
- If this reagent is successfully synthesized, testing will be incorporated into the current work
- Reviews of other alternative reagents and flowsheet options will continue in parallel with the batch extraction testing

Proposed Hot Demo of Multi Tier Solvent Extraction in FY 2003





- **The Solvent Extraction Test Facility (SETF), located in REDC Building 7920, Cell 5, was designed for hot testing of solvent extraction flowsheets**
- **The SETF contains a spent fuel dissolver, feed adjustment and feed metering tanks, and three 16-stage mixer settler contactors**
- **Capability for stage sampling to enable modeling verification**
- **The SETF has been used to evaluate flowsheets for LWR Spent Fuel, FFTF Spent Fuel, and to evaluate the TRUEX flowsheet at high activity levels**

TRISO-Coated Fuel Processing Material Balance on Fuel Materials

Component/kg	Fuel Elements	Compacts	Particles
Graphite	90	-	-
Filler carbon	20.5	20.5	-
Pyro carbon	4.0	4.0	4.0
Porous carbon	1.8	1.8	1.8
SiC	3.1	3.1	3.1
Fuel + FPs	0.9 + 1.9	0.9 + 1.9	0.9 + 1.9
TOTAL	122.2	32.2	11.7

Dealing with the Carbon in the Most Efficient Way is Key

- It is necessary to process ~120 kg of carbon to recover the fissile content (<1 kg) in each fuel element
- A mechanical head-end is needed to separate the bulk of the carbon from the spent fuel
- Combining the carbon component with other elements should be avoided
  - Combination significantly increases the mass of waste to be dispositioned (CO_2, CF_4, CCl_4, etc.)
  - Gaseous forms of carbon are very expensive to capture and sequester by conventional means

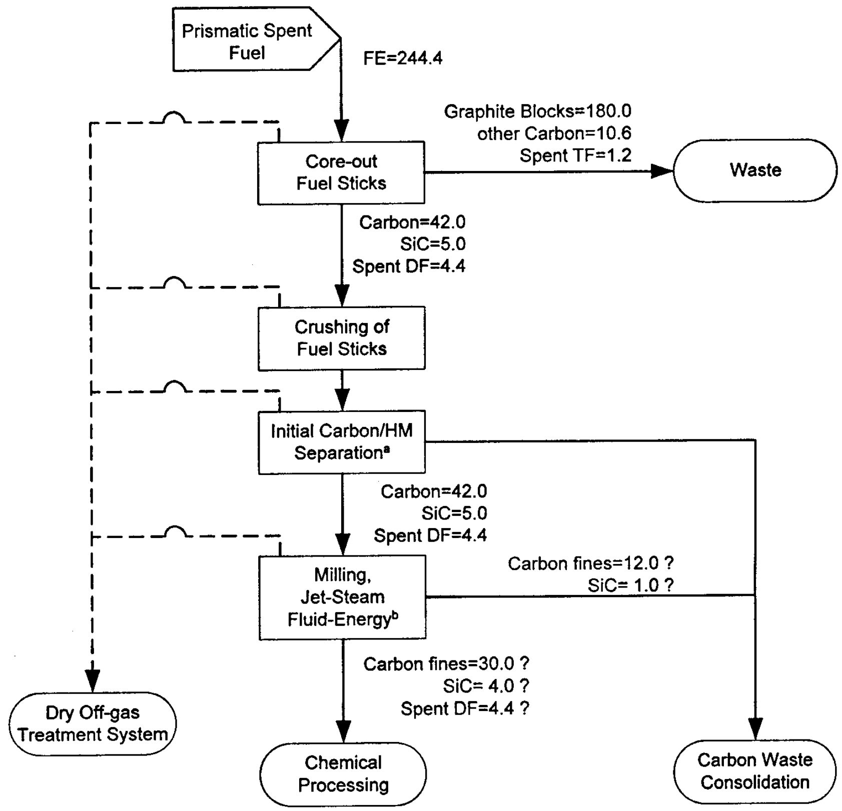
Tentative Pilot-Scale Design for TRISO Fuel Processing

- Basis: Processing rate should be equivalent to spent fuel discharge rate from one HTGR
  - A 600-MW HTGR core contains 340 Fuel Elements
  - 1/3 of core is replaced each year
  - Ratio of DF/TF is TBD (but assumed to be 4:1)
- Pilot-scale facility should process ~2 Fuel Elements/day
  - Assume 200-d/year availability
  - Open 404 fuel channels (top/bottom) to remove compacts
  - Crush/mill ~4800 DFcompacts
  - Separate ~47 kg of (C + SiC) from ~4.5 kg oxide (TRU + FP); TRU accounts for ~1.4 kg

Mechanical Head-End

Pilot scale,

Flow rate in kg/d



[a] Solid/solid separation may be necessary; carrying step until it is proven it is not needed

[b] The steam-jet fluid-energy mill has some separation capability to be determined

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Potential Collaboration with GrafTech

- GrafTech R&D Center possesses relevant industrial experience in
  - Carbon technology and nuclear-grade graphite
  - Crushing and milling
  - Acid leaching
  - Filtering of fine carbon slurries
  - Binding, compacting, and shaping
- There appears to be a strong basis for collaboration in the development of the head-end processes
- Can GrafTech's experience be adapted to hot cell environments?
- What level of participation does GrafTech desire?

Conclusions from GrafTech Visit

- Grinding and milling routine industrial scale (60 tons a day)
  - Rollers for coarse grinding
  - Steam-jet toroidal mill (to micron-range particles)
  - Easy to scale down
  - Very low maintenance (24 h/365 d continuous)
- Routine industrial scale acid leaching, washing and drying
  - Concentrated HNO_3 and H_2SO_4
  - Very low maintenance
- Multistage solid/liquid separation
  - Belt filters with “traveling” high vacuum suction
  - Annual replacement of belts
- Easy to scale down

Wastes Must Be Converted into an Acceptable Waste Form

- Carbon-fine wastes contain multiple impurities
  - SiC fragments
  - Noble metal fission products
  - Water and nitrates
- Repository waste form requirements
  - Stable waste form (low leach rate)
  - No volatiles (water, nitrates, organics, etc.)
  - No fine particles

(Potential Processing Option for Wastes)

- Final waste form: carbon block
- Processing options
  - Add binding agents
  - Compact
  - Sinter (remove water, organics, nitrates)
- Issues
  - Allowable loadings of impurities in graphite
  - Required temperatures
  - Avoidance of secondary wastes

Proposed Schedule for Work Beginning in FY 2003

Month	Work Element
1–9	Dissolution/leaching and carbon washing using mixtures prepared with cold surrogate powders; prepare sintered surrogates, solid/solid separation
7–18	Tests with coated surrogate particles
16–24	Demonstrate process line, at bench-scale, using actual compacts
24	Complete development to reach conceptual design stage
25	Initiate pre-pilot plant design of hot-cell scale demonstration process

FY 2003 Planning
WBS 1.24 Separations

Task	Budget ($ K)	Cumulative ($ K)
Front End (Radioiodine, SX Demo)	1000	1000
Back End (Nitrate-to-Oxide, SANEX Evaluation)	1250	2250
TRISO Head-End (Disassembly/Dissolution)	1250	3500
FLEX Evaluation	500	4000
Waste Form Development (U, Carbon)	500	4500